Solvation Effect in Quenching of Exciplex Emission

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Quenching of exciplex emission in a solution of benzene containing pyrene/anthracene and dimethylamine/diethylamine on the addition of polar solvents (dielectric constants > 30) is due to solvation of exciplexes. However, quenching on the addition of polar solvents with dielectric constants < 30 is due to ionic dissociation of exciplexes.

Increasing solvent polarity results either in a complete quenching of the exciplex band to the red with concomitant decrease in intensity. The decrease in intensity in polar solvents has been attributed to the formation of dissociated radical ions\(^1\) from the exciplexes. The red shift in exciplex emission band with increasing solvent polarity has been attributed to Onsager’s reaction field effect. Recently, Chandross and Thomas\(^2\) have proposed that the most of the spectral change can be explained on the basis of formation of 1:1 non-fluorescent complexes of exciplexes with solvents. In this note we have been able to bring out fresh evidence for formation of such non-fluorescent complexes between pyrene and dimethylamine (DMA) and diethylamine (DEA) as well as between anthracene and DMA and DEA.

When to a solution of pyrene - DEA or DMA in benzene, a polar solvent like dimethylformamide (DMF) is added gradually in increasing amounts, very little new shift in exciplex emission band is observed but the emission is strongly quenched. Quenching follows Stern-Volmer relation indicating 1:1 interaction between exciplex and polar solvent. Further the various emission curves obtained at different DMF concentrations intersect at one specific wavelength (isobestic point) indicating the existence of a 1:1 complex again. Similar results are obtained when other polar solvents like acetonitrile and dimethyl sulphoxide are added to a solution of pyrene-DEA system in benzene. Anthracene-DMA/DEA systems also show a similar behaviour. It is worth noting that for this effect to be operative the dielectric constant of the polar solvent must be > 30. In solvents of lower dielectric constants (such as acetone and propanol) both the shift and quenching are observed. This has been shown to be due to dissociation of ion pairs into radical ions as a result of increase in photoconductivity of the solution containing the solvent.

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References